Materials and Methods for the Production and Purification of

Chlorofluorocarbons and Hydrofluorocarbons

FIELD OF INVENTION

[0001]   The present invention is directed to synthetic production methods, as

well as, synthetic and physical separation methods. More particularly the present

invention is directed to methods for efficiently manufacturing selective isomers of

chlorofluorocarbons and hydrofluorocarbons from aliphatic, olefinic or partially

halogenated hydrocarbons.

BACKGROUND OF THE INVENTION

[0002]   Since the beginning of global warming concerns, chlorofluorocarbon manufacturers have had to produce compounds that perform substantially the same as fully halogenated chlorofluorocarbons without the adverse environmental impact. Only through the introduction of these new compounds have their environmental impact been completely understood. In certain instances, some of these new compounds have been removed from the marketplace. These types of issues make the flooding agent, extinguishing, propellant and refrigerant production industry a dynamic and ever-changing marketplace where processes for the production of chlorofluorocarbons and fluorocarbons are advancing quickly to accommodate both environmental as well as economical requirements.

[0003]   Some useful compounds in this area include both saturated and unsaturated fluorocarbons, such as 1, 1, 1, 2, 3, 3, 3-heptafluoropropane (CF_3-CFH-CF_3, HFC-227ea), 1, 1, 1, 2, 2, 3, 3-heptafluoropropane (CF_3-CF_2-CHF_2, HFC-227ca) and hexafluoropropene (hexafluoropropylene, HFP, CF_3-CF=CF_2, FC-1216). One well known method of synthesizing these compounds begins with the chlorofluorination of propane, propylene or partially halogenated C-3 hydrocarbons with hydrogen fluoride (HF) and chlorine (Cl_2) in the presence of a metal-containing solid catalyst. Examples of this chlorofluorination step can be

found in U.S. Patents 5,057,634 and 5,043,491 to Webster. As taught by Webster, the chlorofluorination step produces a number of saturated perhalogenated chlorofluorocarbons, including: (A) $C_3Cl_5F_3$; (B) $C_3Cl_4F_4$; (C) $C_3Cl_3F_5$; (D) 1,2-dichlorohexafluoropropane (CF_3-$CClF$-$CClF_2$, CFC-216ba); (E) 2,2-dichlorohexafluoropropane (CF_3-CCl_2-CF_3, CFC-216aa); (F) 1-chloroheptafluoropropane ($CF_3CF_2CClF_2$, CFC-217ca); (G) 2-chloroheptafluoropropane ($CF_3CClFCF_3$, CFC-217ba); and (H) octafluoropropane (CF_3-CF_2-CF_3, FC-218). While the FC-218 is useful and can be separated from other perhalogenated reaction products, it is not an efficient or economical intermediate in the synthesis of HFC-227ea, HFC-227ca or FC-1216. As indicated in the '491 patent, the predominant reaction products resulting from the chlorofluorination of propane with HF and Cl_2 is CFC-216aa, which is fluorinated and then dehalogenated to hexafluoropropene (FC-1216).

[0004]   Due primarily to environmental as well as toxicological concerns, demand is increasing for isomerically pure chlorofluorocarbons and hydrofluorocarbons. Teachings such as those described above cannot begin to address these issues and concerns because efficiency of production as well as isomeric purity were not contemplated. Prior art of similar chemistry does not allow for the exclusive production of the HFC-227ea, but only as a mixture or by-

product with FC-1216. The unsuitability of FC-1216 for a fire suppressant does not make this a viable or efficient route.

[0005]   A need exists to develop a method of chlorofluorinating inexpensive C-3 reactants that eliminates one or more by products of chlorofluorination, particularly FC-218 and undesired isomers which cannot be recycled to produce HFC-227ea or HFC-227ca. Moreover, a long felt need exists for extending the lifetime of catalysts used in these reactions.

[0006]   Furthermore, the reaction products generated from these steps require purification. U.S. Patents 6,018,083 to Manogue and 6,211,135 to Miller respectively teach the partial separation (azeotropes) of chlorofluorocarbons C_3ClF_7 (CFC-217) and $C_3Cl_2F_6$ (CFC-216) from HF. These references demonstrate the practical difficulty of separating reaction product mixtures with conventional distillation techniques. The formation of azeotropes requires the use of subsequent or expensive distillation techniques to produce a pure product that can be used as a final product or as an intermediate reactant. A need remains for processes that separate chlorofluorination reaction products without forming azeotropes.

[0007]   The present invention provides processes for the chlorofluorination of aliphatic, olefinic or partially halogenated hydrocarbons in the presence of a

catalyst that results in the substantial elimination of FC-218 as a by-product in the chlorofluorination reaction and that efficiently converts the starting material to the desired isomer. The present invention also provides processes for the efficient purification of reaction product streams.

SUMMARY OF INVENTION

[0008]   One embodiment of the present invention is directed to a process for the manufacture of HFC-227ea, including a novel and highly selective method of preparing a CFC-216aa intermediate by chlorofluorinating C-3 reactants with HF and Cl_2 without the formation of substantial or even detectable amounts of FC-218 or undesired isomers.

[0009]   In accordance with the present invention, the C-3 reactants are chlorofluorinated in a first step with hydrogen fluoride and chlorine in the presence of a metal containing catalyst at a first temperature. The reaction products from this first step are then fluorinated with hydrogen fluoride at a second temperature resulting in an unexpectedly high yield of CFC-216aa without the formation of FC-218.

[0010]   One aspect of the present invention is to provide a method of manufacturing a CFC-216aa intermediate by chlorofluorination of C-3 reactants such as aliphatic, olefinic or partially halogenated hydrocarbons having at least three carbon atoms, wherein the process provides new and unexpected selectivity for the CFC-216aa reaction product.

[0011]   Another aspect of the present invention provides a method of

manufacturing a CFC-216aa intermediate for preparing CFC-217ba and

subsequently preparing HFC-227ea with excellent selectivity and yield, without

the formation of FC-218 or undesired isomers.

[0012]   Another embodiment of the present invention includes a process step

for hydrodehalogenating CFC-217ba to produce HFC-227ea by contacting CFC-

217ba with H_2 in the presence of a metal containing catalyst. According to another

embodiment of the present invention, the hydrodehalogenation step is provided as

just described, with the addition of water to prolong catalyst life.

[0013]   The present invention also provides a process for separating the

isomers HFC-227ea and HFC-227ca by combining the isomeric mixture with a

chlorofluorocarbon and subsequently separating the mixture by distillation. In one

embodiment the chlorofluorocarbon is CFC-217ba.

[0014]   Another process according to the present invention provides for the

purification of halogenation reaction products into HF and chlorofluorocarbons. In

a more specific embodiment, the halogenation reaction product includes CFC-

216aa.

[0015] Still another process for separating halogenation reaction products is provided wherein the reaction products are combined with water and cooled to a sufficient temperature to form a gas phase and top and bottom liquid phases. According to this embodiment, the gas phase contains primarily C-3 chlorofluorinated compounds having at least six fluorine atoms, the top liquid phase is primarily an aqueous liquid phase and the bottom liquid phase contains C-3 chlorofluorinated compounds having less than six fluorine atoms.

[0016] An additional process according to this invention provides for separating C-3 chlorofluorinated compounds from a halogenation reaction product. One embodiment of this invention includes the adjustment of a halogenation reaction product to a sufficient temperature to separate the reaction product into three phases; an upper gas phase and top and bottom liquid phases wherein the upper gas phase contains primarily HCl, the top liquid phase contains HF and the bottom liquid phase contains essentially acid-free C-3 chlorofluorinated compounds;

[0017] In still another process of the present invention methods are provided for synthetically increasing the isomeric purity of a mixture. According to one embodiment, an isomeric mixture of C-3 chlorofluorinated compound isomers is heated in the presence of a catalyst to a sufficient temperature to increase the

isomeric purity. In a more specific embodiment, the C-3 chlorofluorinated compound isomers are CFC-217ba and CFC-217ca.

[0018]   In still another embodiment of the present invention a process is provided for selectively halogenating isomers within an isomeric mixture. In a particular embodiment, the isomeric mixture is exposed to Cl_2 in the presence of a catalyst at a sufficient temperature to halogenate at least one isomer. Preferably the isomeric mixture includes the isomers HFC-227ea and HFC-227ca.

[0019]   The above and other embodiments, aspects, alternatives and advantages of the present invention will become more apparent from the following detailed description of the present invention taken in conjunction with the drawings.

DESCRIPTION OF THE FIGURES

[0020]   Figure 1 is a schematic representation of one embodiment of the present invention.

[0021]   Figure 2 is a graphical representation of the isotherms observed during the processes of the present invention.

[0022]   Figure 3 is a block diagram of an embodiment of Step I according to the present invention.

[0023]   Figure 4 is a block diagram of an embodiment of Step II according to the present invention.

[0024]   Figure 5 is a block diagram of an embodiment of Step III according to the present invention.

[0025]   Figure 6 is a block diagram of an embodiment of Step IV according to the present invention.

[0026]   Figure 7 is a graphical representation of the increased catalyst life observed in an embodiment of Step IV performed according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027]   For the purposes of promoting an understanding of the principles of

the invention, reference will now be made to the embodiments illustrated in the

drawings and specific language will be used to describe the same. It will

nevertheless be understood that no limitation of the scope of the invention is

thereby intended. The invention includes any alterations and further modifications

in the illustrated devices and described methods and further applications as would

be conveyed thereby to one skilled in the art to which the invention relates.

[0028]   Referring now to **Fig. 1**, this invention provides processes for the

production of chlorofluoropropanes and fluoropropanes from aliphatic, olefinic, or

partially halogenated hydrocarbons having at least three carbon atoms. Other

embodiments of this invention provide specific processes for hydrodehalogenating,

isomer and reaction product purification. Selected embodiments of this invention

will be described in turn beginning with the broad chemical process steps used to

produce selected chlorofluorocarbons and fluorocarbons.

[0029]   In part, this invention stems from the discovery that the majority of

the isomer in the final chlorofluorocarbon or hydrofluorocarbon product originates

as an undesired isomer which forms in the initial reactions. This isomer and its

downstream counterparts are passed to subsequent reactions undergoing the same

chemical transformation as the desired isomeric material. Fortunately, CFC-216ba and its downstream counterparts, have different reaction profiles allowing for their reduction with each subsequent step. Unlike CFC-217ca and HFC-227ca, CFC-216ba is not a "dead end" isomer. A majority of this material is directly converted to the desired isomer CFC-217ba in subsequent steps performed in accordance with the present invention.

[0030] Without being confined to any theory, the formation of the undesired isomer takes place in these early reactions by the premature fluorination of the geminal C-2 carbon of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. The production of CFC-216ba is but just one example of this type of chemistry.

[0031] Referring now to **Fig. 2**, formation of excess amounts of CFC-216ba in Step I has been observed when the reaction is allowed to exotherm excessively. The large amounts of energy released during this exotherm are probably the ultimate reason for excess CFC-216ba isomer formation. When these types of conditions are allowed to prevail, ratios as low as 2:1 CFC-216aa:CFC-216ba can be observed in these early reaction streams.

[0032] During the course of the present invention, it was discovered that one way to control this phenomenon was to carefully operate the initial halogenations

so as to avoid uncontrolled exotherms. The reactor used according to the present invention has the ability to use cool heat transfer oil and includes conventional chemical and engineering controls to insure suppression of exotherms. In another aspect of the present invention, HF can be replaced as the main diluent for the reaction. **Figs. 3-4** show a schematic flow diagram for a process according to the present invention that includes a two temperature zone chlorofluorination of a C-3 reactant selected from propane, propylene, partially halogenated C-3 acyclic hydrocarbons, and mixtures thereof, with hydrogen fluoride and chlorine in the presence of a chlorofluorination catalyst. The process is highly selective in the production of CFC-216aa, without the formation of any significant amount of FC-218(0 to less than 0.5 percent by weight). The high yield and selectivity of the process of the present invention in the synthesis of CFC-216aa is very advantageous for the subsequent production of HFC-227ea as discussed below.

[0033] The present invention provides two step processes for efficiently producing CFC-216aa. The chemical steps are the sequential replacement of hydrogen with chlorine and the subsequent partial replacement of chlorine with fluorine atoms. Multiple products are formed with intermediate fluorinated materials being the majority. Careful temperature control minimizes by-product

formation. Typical reaction products include C-3 molecules with 2 to 7 fluorine

atoms, the rest being chlorine. The cracking of the C-3 backbone to form C-1 and

C-2 materials as undesired impurities is also observed. According to one

embodiment, the output of Step I will be fed directly into Step II as shown in

Fig. 4, which is run at a higher temperature.

[0034]   Individual reactants may be fed under flow control to vaporizer(s) 14,

as shown in **Fig. 3**. The vaporized chlorine and HF are mixed and fed into a

superheater of Step I. It has been determined that careful mixing of the reactants

and temperature regulation helps to control reaction exotherms and lack of control

leads to the formation of undesired by-products arising from cracking the C-3

backbone.

[0035]   The predominant reaction occurring in chlorofluorination Steps I and

II can be summarized, as follows, with high selectivity in the production of CFC-

216aa:

$$CH_3CH_2CH_3, CH_3CH=CH_2 \text{ and/or } C_3H_yX_z + HF + Cl_2 \rightarrow CFC\text{-}216aa + HCl$$
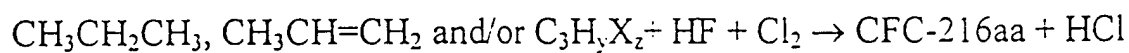
$$(X = \text{halogen; } y = 0\text{-}8, z = 8\text{-}y; \text{ or } y = 0\text{-}6, z = 6\text{-}y).$$

[0036]   The process includes a first step wherein C-3 reactants selected from

the group consisting of aliphatic, olefinic or partially halogenated hydrocarbons

having at least three carbon atoms are contacted with Cl_2 and HF in the presence of a metal containing catalyst. As illustrated in **Fig. 3**, this reaction is preferably performed in the gas phase by the careful mixing of C-3 reactants with a mixture of hydrogen fluoride (HF) and chlorine (Cl_2) in the presence of a metal containing catalyst at a sufficient temperature to form perhalogenated compounds.

[0037] In one embodiment of the present invention, the C-3 reactant is selected from the group consisting of aliphatic, olefinic and/or partially halogenated hydrocarbons, premixed with a mixture of hydrogen fluoride, and then mixed with chlorine before entering chlorofluorination reactor 16 containing a fixed bed of metal containing catalyst.

[0038] Aliphatic hydrocarbons having at least three carbon atoms are known to those skilled in the art to be alkanes, hydrocarbons characterized by a straight or branched carbon chain. These types of compounds include propane. Olefinic hydrocarbons having at least three carbon atoms are known to those having ordinary skill in the art to be unsaturated aliphatic hydrocarbons having at least one double bond. These types of compounds include propene. Partially halogenated hydrocarbons having at least three carbon atoms are known to those having ordinary skill in the art as aliphatic or olefinic hydrocarbons wherein one or more hydrogens have been replaced by halogens.

[0039]   According to one embodiment of the present invention, the HF and C-3 reactants are premixed before being combined with the chlorine gas and conveyed into a chlorofluorination reactor. It is preferred to premix (dilute) the C-3 reactant with the hydrogen fluoride reactant prior to combining the HF/C-3 gas reactants with the chlorine gas reactant in order to minimize the potential reaction of the C-3 reactant, e.g., propane and/or propylene with concentrated chlorine gas. Accordingly, at least one of the C-3 reactant or the chlorine, preferably both the C-3 reactant and chlorine, should be diluted with hydrogen fluoride prior to combining the C-3 reactant with the chlorine gas.

[0040]   In one embodiment of the present invention the HF is anhydrous. It has been determined that recycled or reagent grade HF may used. The type of HF used to perform this aspect of the invention is not critical and specific types and qualities will be recognized by those skilled in the art. The Cl_2 likewise is a matter of choice to those having skill in the art. In one embodiment, technical or pure-grade anhydrous Cl_2 is utilized.

[0041]   The chlorination of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms is a highly exothermic reaction which may be controlled through the use of excess quantities of hydrogen fluoride,

-16-

a diluent, or a external heat transfer medium together or in combination, to absorb the heat evolved and to maintain temperature control of the mixture.

[0042]   To reduce the impact of exotherms, preferably, a stoichiometric excess of hydrogen fluoride is maintained in order to minimize decomposition of the C-3 reactant to C-1 and C-2 by-products, and the formation of the less desired CFC-216ba, preferably about 6 to about 64 moles of HF per mole of C-3 reactant. It is preferred to provide an excess of chlorine gas as well, preferably about 8 to about 10 moles of Cl_2 per mole of C-3 reactant, but an excess of Cl_2 is not required. In a preferred embodiment, the ratio of Cl_2 to C-3 reactants can be 8.2:1. The molar ratio of HF to Cl_2 is from about 0.75:1 to about 8:1. Perferably, the molar ratio of HF to Cl_2 is about 4:1. Moreover, in another embodiment a diluent may be added to the reaction to decrease undesired isomer and formation of cracking materials.

[0043]   Preferably the chlorofluorination reactor 16 used to perform this invention is maintained at a reaction pressure of about 0 psig to about 750 psig, preferably about 0 psig to about 750 psig and at a temperature in the range of about 150°C to about 450°C, and preferably about 220°C. For best results, residence time in chlorofluorination reactor 16 should be in the range of about 0.5 seconds to about 30 seconds and preferably about 5 to about 10 seconds. The resulting

reaction mixture coming out of Step I shown in **Fig. 3** is rich in $C_3Cl_4F_4$ and

$C_3Cl_3F_5$ but will also contain CFC-216aa and many other under fluorinated

compounds. Preferably reaction products of this first step are conveyed directly to

Step II, as shown in **Fig. 4**, however it is recognized that the reaction products of

Step I, as shown in **Fig. 3**, may be further purified or supplemented prior to

continuing on to Step II. A main goal in Step II is the selective fluorination of

these under-fluorinated compounds to the desired isomer CFC-216aa.

[0044] The second step in this process replaces all of the terminal chlorine

substituents with fluorine to produce CFC-216aa. According to one aspect of the

present invention this is accomplished through the use of high temperature reaction

conditions, excess HF, and a metal containing catalyst.

[0045] As shown in **Fig. 4**, the Step I reaction stream is directly fed into a

superheater 24. Optimally, this stream is then fed to Step II reactor 26. Again, as

before in Step I, careful temperature regulation is used to control the reaction.

[0046] The second reaction can take place either in the same reactor as Step I

or, preferably, in a second reactor. The second step is carried out at a higher

temperature than the first step with a stoichiometric excess of hydrogen fluoride.

According to one embodiment a stoichiometric excess of chlorine can be used to

ensure chlorofluorination of the Step I reaction products.

[0047] Preferably, Step II reactor 26 is a fixed-bed reactor having a metal containing catalyst, maintained at a reaction pressure of about 0 psig to about 750 psig and preferably about 100 psig, and at a temperature higher than the temperature required in Step I. Step II occurs at a temperature ranging from about 300°C to about 550°C, and preferably at about 470°C. It is preferred that the molar ratio of reactants in Step II, should be maintained at about 6 to about 64 moles of hydrogen fluoride per mole of perhalogenated compounds. As in Step I, the source and quality of anhydrous HF used in Step II is not critical. It is to be understood by those skilled in the art that anhydrous, recycled, and/or differing grades of HF can be used in Step II. As in Step I, a diluent may be added to control exotherms and increase isomeric yield.

[0048] The metal containing catalyst used in Step I or Step II can be any known catalyst useful for reacting C-3 reactants or perhalogenated compounds with HF and/or Cl_2, including those described in U.S. Patent Nos. 5,177,273 and 5,057,634 to Webster, hereby incorporated by reference. These catalysts include catalysts consisting essentially of chromium; catalysts consisting essentially of chromium oxide in combination with a support (e.g. refractory oxide); catalysts consisting essentially of chromium oxide modified with up to about 10 percent by weight based upon the weight of chromium in the catalyst of metal selected from

the group consisting of manganese, iron, cobalt, nickel, copper, zinc, other metals and mixtures thereof; and catalysts consisting essentially of chromium oxide in combination with a refractory oxide and modified with up to about 10 percent by weight based upon the weight of chromium in the catalyst of metal selected from the group consisting of manganese, iron, cobalt, nickel, copper, zinc, other metals and mixtures thereof. Chromium oxide catalysts and their preparation in the art of perhalogenation are well known.

[0049]   The chromium oxide and metal modified chromium oxide catalysts may be unsupported or supported. Catalysts consisting essentially of either chromium oxide or metal modified chromium oxide in combination with a support (e.g., alumina) may be prepared by conventional procedures (e.g., impregnation of the support using a suitable soluble chromium salt alone or in combination with a suitable soluble salt of the metal modifier). In addition, catalysts of this invention can also be prepared by co-precipitation methods, which are known in the art. Typically for refractory oxide containing catalysts, the refractory oxide constitutes from about 80 to 99.5 weight percent of the catalyst.

[0050]   Catalysts consisting essentially of fluorinated chromium oxide, or fluorinated chromium oxide in combination with a refractory oxide, or fluorinated metal modified chromium oxide or fluorinated metal modified chromium oxide in

combination with a refractory oxide may also be used. Indeed, the catalysts are preferably fluorinated prior to use for the halogenation process of this invention by treatment with a suitable fluorine-containing compound (e.g., HF, SF_4, CCl_3F, CCl_2F_2, CHF_3, or $CCl_2F-CClF_2$) at elevated temperatures. Pretreatment of catalysts containing refractory oxides such as alumina are considered particularly useful. Such treatments are well known to the art. The treatment with HF or other fluorine-containing compound can conveniently be done in the same reactor which is to be used for the production of the selected halohydrocarbon product(s). Iron and nickel containing catalysts, specifically iron chloride and nickel chloride catalysts, supported or unsupported may be employed as well.

[0051]   The catalysts of this invention can undergo changes in composition and/or structure during use. One skilled in the art will recognize, for example, that during use the catalyst may be in the form of an oxyfluoride, an oxychloride, an oxychlorofluoride and/or an oxide, and/or may have a different crystalline structure from the catalyst charged to the reactor. Charging the reactor with these compounds (e.g., an oxyfluoride, etc.) or with any compound(s) convertible to these compounds under reaction conditions is considered an equivalent procedure within the scope of this invention.

[0052]   In this and the other reaction sequences, reaction with HF includes either high temperature vapor phase reaction or lower temperature reaction in the presence of a liquid phase catalyst such as $SbCl_5$ /HF or SbF_5; the vapor phase process is preferred.

[0053]   Two metal containing catalysts that have been found to be particularly useful for the chlorofluorination reactions include:

[0054]   (1) $FeCl_3$ on a support, particularly active carbon, that is dried and then fluorinated, e.g., with HF, preferably an HF/N_2 mixture, with or without O_2, at about 200°C to about 270°C and then treated with HF, with or without O_2 or Cl_2 activation, within the range of about 270°C to about 320°C. It is preferred that the percent by weight of $FeCl_3$ in the metal containing catalyst be in the range of about 2% to about 36% by weight on a catalyst support, which is preferably activated carbon, preferably at about 5% to about 10% by weight $FeCl_3$. It is useful to fluorinate the metal containing catalyst for a period of at least about 2 hours, preferably about 2 to about 16 hours, more preferably about 8 hours, gradually increasing the temperature within the range of from about 200°C to at least the chlorofluorination reaction temperature, e.g., up to about 320°C; and

[0055]   (2) $CrCl_3$, particularly chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) on a support, particularly active carbon, that is dried and then fluorinated, e.g., with

hydrogen fluoride gas (HF), in the same manner as fluorination of the $FeCl_3$ catalyst with or without O_2 or Cl_2 activation.

[0056]   Non-limiting examples 1, 2, and 3 demonstrate the preparation of catalysts suited for the present invention and non-limiting example 4 demonstrates the activation of catalyst suited for this invention.

[0057]   Generally, all fluorination catalyst were prepared by mixing appropriate amounts of the selected metal salt and support (if necessary) in DI water. This mixture is allowed to stand for approximately 0.5 hour and the excess water is filtered off by vacuum filtration. The resulting solid is then dried overnight in a gravity oven at 115°C and then charged to the reaction tubes were it is further dried at 150°C with a inert gas purge and then activated with HF before the reaction feeds are started.

Example 1: FeCl₃/Activated Carbon Catalyst Preparation:

[0058]   Iron (III) chloride hexahydrate (20 grams) was dissolved in deionized water (300 cc). The solution was then mixed into and absorbed by 200 grams of active carbon pellets and air-dried overnight.

Example 2: CrCl₃/Activated Carbon Catalyst Preparation:

[0059]   Chromium (III) chloride hexahydrate (12.6 grams) was dissolved in deionized water (100 cc). The solution was mixed into and absorbed by 75 grams of active carbon pellets and air-dried overnight.

Example 3: NiCl₂/Activated Carbon Catalyst Preparation:

[0060]   Nickel (II) chloride hexahydrate (13.8 grams) was dissolved in deionized water (100 cc). The solution was mixed into and absorbed by 75 grams of active carbon pellets and air-dried overnight.

Example 4: Metal Chloride/Carbon Catalyst Activation Methods:

[0061]   The chlorofluorination catalyst was activated using a chlorofluorination reactor with HF. The following description gives the detailed procedures for three methods of chlorofluorination catalyst activation.

[0062] (a)   The FeCl₃/carbon catalyst of Example 1 was added to both Step I and Step II reactors and the catalyst in each reactor was dried with N₂ and fluorinated with HF/N₂ to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF mole of active metal in the catalyst at 250°C for 9 hours. The

metal containing catalyst in the Step I reactor was then further activated with HF/N_2 to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 285°C for another 14 hours. The metal containing catalyst in the Step II reactor was then further activated with HF/N_2 to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 465°C for another 14 hours.

[0063] (b) The same procedure discussed above in method (a) was performed for drying metal containing catalyst with N_2 and fluorination with HF/N_2. The metal containing catalyst was further activated with 2% by weight O_2 along with HF//N_2 to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst for 12 hours, then another 2 hours without O_2.

[0064] (c) The same procedure was performed for the catalyst activation as described above in method (b) except using 2% by weight Cl_2 instead of 2% by weight O_2.

[0065] For all reactions exemplified herein, except where noted, two 41.6 cc, 0.5 in. (OD), alloy 600 reactor tubes heated with ceramic fiber, radiant heat electric ovens were utilized as reactors. The tubes were utilized alone or in tandem to perform the reaction examples.

[0066]   Non-limiting example 5 demonstrates the results of chlorofluorination, according to the present invention.

Example 5: Chlorofluorination of C-3 Reactants:

[0067]   Step I was conducted according to the parameters indicated in Table 1 below. The reaction products of Step I were conveyed to the Step II reactor. The Step II reaction was also conducted according to the parameters indicated in Table 1.

[0068]   Like Step I, Step II was performed with a fixed-bed reactor containing a metal containing catalyst. The specific types of catalyst are described in Table 1 below. The hydrogen fluoride used in Step I and Step II was anhydrous liquid HF that was vaporized to provide anhydrous HF gas. The results of the present example are shown below in Table 1.

Table 1. Step I and Step II with Metal Chloride Catalyst Systems

Catalyst	Reactant Flows HF/Cl$_2$/C$_3$H$_8$ (cc/min)	Reactants Mole Ratio (HF/Cl$_2$/C$_3$H$_8$)	Step I Run Conditions		Step II Run Conditions		Results*	
			Temperature (C)	Contact Time(sec)	Temperature (C)	Contact Time (sec)	%CFC-216aa	% CFC-216ba
FeCl$_3$/ Activated Carbon	109.1/44.8/3.2	49/20/1	400	6.4	450	5.8	79.8	nd
CrCl$_3$/ Activated Carbon	106.5/43.9/2.5	48/20/1	300	7.8	480	5.9	81.9	6.3
NiCl$_2$/ Activated Carbon	137.3/31.1/2.5	61/14/1	300	7	480	5.3	39.6	8.6

nd = Not detected.   *% GC Area

[0069]   As demonstrated in Table 1 above, iron and chromium chloride catalysts are particularly well suited

for use as metal containing catalysts according to the present invention. In particular, when utilizing the iron

catalyst no detectable levels of the undesired CFC-216ba isomer were found.

[0070]   Non-limiting example 6 demonstrates the reaction efficiency of the present invention.

Example 6: Mass Balance Demonstration:

[0071]   Step I was conducted at a temperature of about 280°C with a molar ratio of HF:Cl$_2$:C-3 reactant, 6:9:1. Residence time in the Step I reactor was about 10 seconds. The reaction products of Step I were conveyed to the Step II reactor. The Step II reaction was carried out at about 465°C. Like Step I, Step II was performed with a fixed-bed reactor. The chlorofluorination catalyst used in both halogenation reactors (Step I and Step II) was a supported chromium containing catalyst.

[0072]   The reaction products, contained predominantly CFC-216aa, hydrogen fluoride and hydrogen chloride gas, and were conveyed into a central portion of a strip column for HCl removal.

[0073]   The chlorofluorination reaction products were collected for analysis by gas chromatography. The amount of the specific compound is indicated in terms of chromatographic area percent. For this, and the following examples, area percent is consistently utilized to demonstrate the advantages of the present invention.

[0074]   The reaction products were collected for analysis and reported in

Table 2 below.

Table 2. Mass Balance of Reactants and Products of the Present Invention

Total Feed Materials	C_3H_8	6.8 lbs
	Cl_2	101.75 lbs
	HF	19.2 lbs
Total Products Collected	HCl	90.4 lbs
	$C_3Cl_2F_6$	23.85 lbs
	Underfluorinated compounds	7.55 lbs.
Recovery		~95%

[0075]   As Table 2 shows, (mass balance) of the present invention is good at

approximately 95% recovery of reactants.

[0076]   Non-limiting example 7 demonstrates the flexibility of starting

material selection of the present invention.

Example 7: Use of Varying Starting Materials and Reagent Proportions:

[0077]   Tandem alloy 600 pipes were charged with supported chromium

oxide catalyst. Liquid HF was vaporized and the HF vapor was then mixed with

propylene/propane gas through an in-line static mixer and then mixed with Cl_2 at

the top of the Step I pipe, according to the parameters shown below in Tables 3 below. The reaction products from the Step I pipe were conveyed to the Step II pipe and the Step II reaction products were fed into a strip column to separate HCl, Cl_2 and light components from HF, CFC-216aa and heavy components that were removed from the bottom of the strip column. The strip column bottom components were then fed into a phase separator to separate HF from organic materials, including $C_3Cl_2F_6$ for analysis by gas chromatography. Recovered or recycle HF was fed back to the Step I pipe vaporizer. The underfluorinated organic materials were collected and recycled back to the Step I pipe for further fluorination.

[0078]   The results of using propane or propene as a C-3 reactant is shown below in Table 3, propene (C_3H_6, Runs A and B) or propane (C_3H_8, Runs C and D) as the raw material (C-3 reactant) for the present invention. The results of using varying proportions of reactants and the effects of additions of a diluent are shown below in Table 4. The exotherms observed during run conditions dictated in Table 4 are demonstrated in Figure 2.

Table 3. Use of Either Propane or Propylene as a C-3 Reactant

Example	Step I Temp. (°C)	Step II Temp. (°C)	Pressure (psig)	Flow Rates HF (g/min)	Cl₂ (g/min)	C₃H₆ (g/min)	Ratio HF/C₃H₆	(moles) Cl₂/C₃H₆	G.C.% C₃Cl₃F₆
A	227.8	465	55	29.77	28.38	2.27	27.54	7.40	71.95
B	275	465	55	30.2	31.17	2.12	29.92	8.7	72.21
				Flow Rates HF (g/min)	Cl₂ (g/min)	C₃H₈ (g/min)	Ratio HF/C₃H₈	(moles) Cl₂/C₃H₈	
C	282.5	465	55	28.46	31.28	2.02	31.00	9.60	68.38
D	282.7	465	55	30.6	31.02	2.27	29.66	8.47	71.96

[0079]   As Table 3 above demonstrates, the present invention is equally efficient regardless of the starting material. It was concluded that the selection of an under halogenated compound as a C-3 reactant will demonstrate similar results.

TABLE 4 – DEMONSTRATION OF UTILIZING VARYING REACTANTS AND DILUENTS

	Step I Reaction Parameters				Step II Reaction Parameters				Results		
RUN	Diluent (X)	TEMP. (C)	CONTACT TIME (seconds)	MOLE RATIO (X:HF:Cl₂:PROP.)	MOLE RATIO HF:Cl₂	TEMP. (C)	CONTACT TIME (seconds)	MOLES HF:PROPANE	% CFC-216aa IN GAS STREAM	% CFC-216ba IN GAS STREAM	SELECTIVITY (%)
A	none	200	10.2	0 : 4.7 : 7.4 : 1.0	0.64	450	3.7	15.1	51.0	4.16	56.4
B	CFC-217ba	200	9.7	1.6 : 4.8 : 6.3 : 1.0	0.77	450	3.6	15.2	55.5	5.79	73.8
C	CFC-217ba	200	10.1	4.0 : 5.1 : 7.9 : 1.0	0.65	450	3.7	19.2	61.6	n/d	87.5
D	none	200	9.2	0 : 5.3 : 4.4 : 1.0	1.20	450	3.4	13.3	13.17	1.74	32.2
E	HFC-227ea	200	11.0	4.3 : 4.6 : 9.1 : 1.0	0.50	450	3.9	20	32.01	18.57	69.9
F	CFC-217ba	260	9.2	2.9 : 4.4 : 6.1 : 1.0	0.72	450	3.7	16.1	72.1	n/d	85.1
G	none	200	10.7	0 : 17.5 : 4.3 : 1.0	4.04	450	3.9	36.2	39.6	n/d	48.5

[0080] As Table 4 above demonstrates, with particular reference to runs C and F, the present invention is highly selective for CFC-216 aa. As in Figure 2, Table 4 demonstrates the exotherms observed are consistent with the formation of undesired isomers.

[0081]   In non-limiting example 8 below, the benefit of combining reagents in a specified order according to the present invention is demonstrated.

Example 8: Raw Material Mixing Effect:

[0082]   Two tests were performed by: (1) using a static mixer to first mix HF with C_3H_8 and then mix the HF/C_3H_8 mixture and Cl_2 in another mixer before the Step I reactor; and (2) first mixing the HF with Cl_2 using a static mixer, and then adding the HF/Cl_2 mixture to C_3H_8 in another mixer before the Step I reactor. The reaction parameters and results of this example are listed in Table 5 below.

Table 5. Mixing Affect on Product Formation According to the Present Invention

| Example | Step I Temp. (°C) | Step II Temp. (°C) | Pressure (psig) | Flow Rates | | | Ratio (moles) | | $C_3Cl_2F_6$ (GC Area %) |
				HF (g/min)	Cl_2 (g/min)	C_3H_8 (g/min)	HF/C_3H_6	Cl_2/C_3H_6	
(a) mixing HF/C_3H_8		(b) mixing Cl_2							
8A	274.6	465	55	34.39	38.09	2.02	37.45	11.69	61.86
8B	274.5	465	55	36.40	36.52	1.97	40.65	11.49	60.49
(a) mixing HF/Cl_2		(b) mixing C_3H_8							
8C	274.8	465	55	32.90	35.18	1.89	38.30	11.54	63.01
8D	275.7	465	55	32.63	34.62	1.89	37.98	11.35	63.34

[0083]   As Table 5 demonstrates, the combination of reactants plays no role in the overall selectivity of $C_3Cl_2F_6$. Even though it appears conversion is increased it is probably due to increased residence time in the reactor, rather than order of mixing of reactants.

[0084]   Another process according to the present invention provides for purifying halogenation reaction products. For purposes of the present invention, halogenation reaction products encompass those reaction products as described above and refers to reaction products of reactions wherein chlorine and/or fluorine atoms replace hydrogen or halogen atoms along carbon atom backbones. In most cases the products of these reactions include HF and organic chlorofluorinated compounds. In another embodiment of the present invention the C-3 chlorofluorinated compounds have at least six fluorine atoms.

[0085]   Referring to **Fig. 4**, according to one embodiment of the present invention to separate HF from C-3 chlorofluorinated compound reaction products, the temperature of the chlorofluorination reaction product is reduced to a sufficient point within phase separator 28 to separate the reaction products into separate top and bottom liquid phases. According to one embodiment, the temperature used to accomplish this separation is from about -30°C to about -10°C. In a preferred embodiment the temperature is about -20°C.

[0086]   To complete the separation of the HF from the C-3 chlorofluorinated compounds (which can have at least six fluorine atoms) the top phase (formed by lowering the temperature of the chlorofluorination reaction products) is removed to

obtain essentially organic free HF and/or simultaneously the bottom phase is removed to obtain essentially acid free C-3 chlorofluorinated compounds. This separation can be performed on an industrial scale continuously in a unit operation or in a batch operation. Persons skilled in the chemical engineering arts will routinely be able to select the type of apparatus necessary to perform this liquid/liquid phase separation.

[0087]   One of the distinct advantages of this process for separation HF from C-3 chlorofluorinated compounds is that expensive distillation is not required. Nor is there a production of the HF/C-3 chlorofluorinated compound azeotrope. Problems associated with distillation processes and the production of HF/chlorofluorocarbon azeotropes are discussed in U.S. 6,211,135 to Miller, herein incorporated by reference. Referring now to Figure 4., it has been found during the course of the present invention that at low temperatures, the HF phase 30 is virtually free of organic C-3 chlorofluorinated compounds and likewise the organic phase 32 having C-3 chlorofluorinated compounds are virtually free of HF. Moreover, because the separation according to the present invention results in two product streams, either product may without further purification be sent on to additional reaction steps or returned or recycled to previous reaction steps.

[0088]   Because the phase separation of the present invention is performed in the liquid phase, any pressure sufficient to maintain the materials in the liquid phase can be used according to the present invention. Preferred embodiments of the present invention use low temperatures and ambient pressures. However, the resulting nonazeotropic mixtures of HF and organic C-3 chlorofluorinated compounds exist at different temperatures depending on the pressure of the system.

[0089]   The present invention providing for HF/organic separation is demonstrated below by non-limiting example 9.

Example 9: HF/Organic Phase Separation:

A chlorofluorination reaction product including HF, Cl_2 and CFC-216aa was purified according to the present invention. The reaction feed stream included 5.3 lb./min Cl_2 , 0.4 lb./min propane, 0.84 lb./min HF and 11.12 lb./min recycled HF with a reaction product stream containing 75 weight percent CFC-216aa on an acid free basis. The HCl was removed by distillation and the bottoms of the distillation column (HF and organic chlorofluorination reaction products) was cooled and sent to a 200 gallon liquid phase separation tank where it was chilled. The vapor pressure of the mixture in the phase separator was 14.5 psig at 21.8°C. The mixture separated into two phases, a bottom phase and a top phase. The bottom phase comprised a liquid organic phase that was decanted off and

scrubbed and purified to produce pure CFC-216aa. The top phase comprised a liquid HF phase that was decanted off and recycled to a previous reaction step. The organic phase was analyzed and the results are represented in Tables 6 and 7 below.

Table 6. Chlorofluorination Organic Phase Removed from HF According to a Process of the Present Invention

	Area % Cl_2	Area % HF	Area % HCl	Area % Organic
Separated Organic Phase	1.21	0.3872	0.6097	97.79

Table 7. Halogenated Organics Separated from HF According to the Present Invention

Halogenated Organics	Percentage of Total Organics
$CCl_3F\text{-}CClF_3$	not detected
lights	0.05
$C_3Cl_2F_6$	64.59
$C_3Cl_3F_5$	11.82
$C_3Cl_4F_4$	5.75
Heavies	3.65

[0090]   As this example demonstrates the organic phase, once separated according to an embodiment of the present invention, is essentially acid-tree. This allows for the immediate isolation of specific chlorofluorination reaction products without the need for costly and inefficient distillation. Moreover, Table 7 demonstrates that other halogenated organics can be separated from HF according to the present invention. These chlorofluorination reaction products can be

-38-

isolated according to another process of the present invention as herein described next.

[0091]   Another process according to the present invention is the separation of the C-3 chlorofluorinated compounds having at least six fluorine atoms from C-3 chlorofluorinated compounds having less than six fluorine atoms. This separation process is extremely useful in order to maintain the compound purity of chlorofluorinated compounds sought to be produced.

[0092]   According to one embodiment of the present process, a solution comprising C-3 chlorofluorinated compounds having at least six fluorine atoms and C-3 chlorofluorinated compounds having less than six fluorine atoms is provided. This solution is derived from a reaction product or a refined reaction product of a chlorofluorination reaction or the phase separation or distillation product after a chlorofluorination reaction. In one embodiment of the present invention the C-3 chlorofluorinated compounds having at least six fluorine atoms comprises CFC-216aa. However, this invention is not limited to the source of this mixture. According to the present invention, the solution is contacted with the water to form a mixture of organics and water. This may be performed using various blending or mixing apparatuses, the particular type of apparatus is not critical and those skilled in the art will recognize apparatus suited for preparing this mixture.

[0093]   It is preferred that deionized water be added to the solution to obtain the mixture. However, other forms of water can be used having various salt concentrations and/or pH levels. According to another embodiment, the water mixed with the solution comprising the chlorofluorinated compounds may include a basic compound, such as potassium hydroxide. Persons having skill in the art will understand that a compound that is basic is a compound that is more alkaline than other compounds. These are known to those skilled in the art as compounds that when added to water raise the pH of the water from its neutral pH to a higher than neutral pH.

[0094]   According to one embodiment of the present invention, after mixing, the temperature of this water mixture is then adjusted to a sufficient temperature to separate the water mixture into at least three phases, including an upper gas phase containing C-3 chlorofluorinated compounds having at least six fluorine atoms, a top aqueous phase, and a lower liquid phase containing C-3 chlorofluorinated compounds having less than six fluorine atoms. The temperature sufficient to obtain the three distinct phases described above is from about 25°C to about 75°C. The preferred temperature used to obtain these three phases is about 50°C.

[0095]   The above process of separating the C-3 chlorofluorinated compounds alleviates the need for cost intensive and inefficient distillation. The separation of

the C-3 chlorofluorinated compounds can be performed as a continuous phase separation process or as a batch phase separation process, applying techniques known to those having skill in the art of phase separation. The upper gaseous phase can be removed to obtain essentially pure C-3 chlorofluorinated compounds having at least six fluorine atoms while at the same time or, alternatively in a batch process, the bottom liquid phase containing C-3 chlorofluorinated compounds having less than six fluorine atoms can be removed either leaving behind or allowing for the removal of the top aqueous phase. Upon removal, these phases can be further processed or retained as end products. According to one embodiment of the present invention, the chlorofluorinated compounds having at least six fluorine atoms are conveyed to an additional reaction step to increase the number of fluorine atoms present.

Example 10: Separation of Fluorinated Compounds:

[0096]   The containers of crude $C_3Cl_2F_6$ from various production runs of Steps I and II contained $C_3Cl_2F_6$ and numerous other unidentified underfluorinated compounds, and possible small amounts of H_2O, HF, Cl_2, and HCl.

[0097]   Approximately 160 lbs. of crude $C_3Cl_2F_6$ were fed from a heated cylinder to a 15 gallon Halar ® lined scrubber tank. The scrubber tank contained a

level gauge and an external heat tracing with a skin temperature thermocouple. The feed line into the tank was through a dip tube.

[0098]   The tank was initially filled with a 5% KOH/water solution and the temperature of the tank was heated to 50°C. The mixture separated into three phases: an upper, primarily gaseous phase; a top liquid, primarily aqueous phase; and a bottom primarily organic phase. The top gas phase was removed as a vapor stream and fed to a Halar ® lined scrubber. The vent gas was open to a molecular sieve dryer bed which fed into a chilled collection cylinder on a scale. Upon completion of the scrubbing of the $C_3Cl_2F_6$, the underfluorinated organics collected from the bottom phase was approximately 20 lbs. of material. The primary components of this organic liquid were $C_3Cl_4F_4$, and $C_3Cl_3F_5$ and $C_3Cl_2F_6$.

Table 8. Results of Separation of Underfluorinated Separation According to the Present Invention

Separated Phase	Constituents
Vapor	essentially pure $C_3Cl_2F_6$
Bottom	~6% $C_3Cl_2F_6$ and ~94% underflorinated compounds

[0099]   As Table 8 demonstrates, underfluorinated compounds can be efficiently separated from $C_3Cl_2F_6$ according to the present invention.

[00100]   Alone or in combination with Steps I and II above, as shown in Fig. 5, the present invention provides a third reaction step (Step III) for the selective fluorination of $C_3Cl_2F_6$ to CFC-217ba. The predominant reaction occurring in this step is as follows:

$$C_3Cl_2F_6 + HF \rightarrow CF_3\text{-}CFCl\text{-}CF_3 + HCl$$
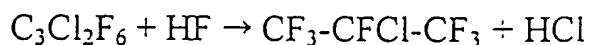
[00101]   Preferably, Step III proceeds in the gas phase with excess anhydrous HF over a metal containing catalyst. According to one embodiment of the present invention, the reactants of Step III are fed under flow control to vaporizer(s) 34. These vaporized reactants include CFC-216aa which are fed to reactor 36.

[00102]   In Step III isomer formation can be controlled by selective fluorination. Since the undesired CFC-216ba contains 2 chlorine atoms it is not technically a "dead end" material. It has been demonstrated that by selective fluorination CFC-216ba will lead to CFC-217ba but CFC-216aa does not readily convert to CFC-217ca. Isomer formation is also effected by conversion.

[00103]   According to one embodiment, the high yield CFC-216aa chlorofluorination product recovered from Step II reaction described previously is mixed with hydrogen fluoride and contacted with a metal containing catalyst. Residence time of Step III is in the range of about two seconds to about 60 seconds, and preferably about 20 seconds to about 30 seconds.

[00104]   Referring to Figure 5, according to one embodiment, reactor 36 is a fixed bed reactor having a metal containing catalyst on a suitable solid support. The metal containing catalyst can be any catalyst known as being useful for the fluorination of C-3 chlorinated hydrocarbons with hydrogen fluoride.

[00105]   Preferred catalysts for the synthesis of CFC-217ba are supported metal containing catalysts. Metals such as iron, zinc, chromium and mixtures thereof are particularly useful as catalysts for the conversion of $C_3Cl_2F_6$ to CFC-217ba. Acceptable results can be obtained with other metal-containing catalysts, provided the temperature, contact time, and other reaction conditions are suitably selected.

[00106]   Suitable catalysts are supported catalysts that are dried and HF/N_2 treated at 250°C, e.g., for 9 hours, and then HF/N_2 treated at 465°C, e.g., for another 14 hours using a stoichiometric excess of HF, e.g., about 1.5-3 moles of HF per mole of active metal in the catalyst. This catalyst activation process can include O_2 or Cl_2 gas at a concentration of about 0.5% to about 5% by weight, e.g., 2%.

[00107]   The catalysts are particularly effective when activated according to one of the following three methods (a), (b), or (c) described below:

-44-

[00108] (a) The catalyst is dried with N_2, fluorinated with HF/N_2 at 250°C for 9 hours. The catalyst is then further activated with HF/N_2 at 465°C for another 14 hours.

[00109] (b) The same procedure is performed for catalyst drying and fluorination as described above in method (a). The catalyst is then further activated with 2% by weight O_2 along with HF/N_2 for 12 hours, then another 2 hours without O_2.

[00110] (c) The same procedure for the catalyst activation as described above in method (b) is used except using 2% by weight Cl_2 instead of O_2.

[00111] Non-limiting examples 11 and 12 demonstrate the preparation of catalysts suited for the present invention and non-limiting example 13 demonstrates the activation of catalyst suited for this invention.

Example 11: FeCl₃/Activated Carbon Catalyst:

[00112] Iron (III) chloride hexahydrate (3.78) moles was dissolved in deionized water (1000 cc). The solution was mixed into and absorbed by 1000 grams of active carbon pellets and air-dried overnight.

Example 12: CrCl₃/Activated Carbon Catalyst:

[00113] Chromium (III) chloride hexahydrate (5.14 moles) was dissolved in deionized water (2100 cc). The solution was mixed into and absorbed by 3000 grams of active carbon pellets and air-dried overnight.

Example 13: Metal Chloride/Carbon Catalyst Activation Methods:

[00114] The catalyst was activated using a fluorination reactor with HF. The following description gives the detailed procedures for three methods of fluorination catalyst activation.

[00115] (a) The FeCl₃/carbon catalyst of Example 11 was added to Step III reactor (herein, the reactor is identical to those reactors described previously) and the catalyst was dried with N₂ and fluorinated with HF/N₂ to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 250°C for 9 hours. The catalyst was then further activated with HF/N₂ to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 465°C for another 14 hours.

[00116] (b) The same procedure discussed above in method (a) was performed for metal containing catalyst drying with N₂ and fluorination with HF/N₂. The metal

containing catalyst was further activated with 2% by weight O_2 along with HF/N2 to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst for 12 hours, then another 2 hours without O_2.

[00117]   (c)   The same procedure was performed for the catalyst activation as described above in method (b) except using 2% by weight Cl_2 instead of 2% by weight O_2.

[00118]   The HF:C-3 reactant molar ratio utilized in Step III is preferably in the range of about 1-30 moles of HF per mole of C-3 reactants and the reaction pressure is in the range of about 0-750 psig, and preferably about 100 psig at a temperature of about 200°C to about 550°C, and preferably about 485°C. Like Steps I and II previous, Step III may combine a diluent with the reactants.

[00119]   By way of non-limiting example 14, a reaction according to an embodiment of the present invention is shown below.

Example 14: STEP III ($C_3Cl_2F_6 \rightarrow$ CFC-217ba):

[00120]   A 2" I.D. x 50" long alloy 600 pipe reactor was heated to 485°C by an electric heater. The reactor was connected to a distillation column, which had a

pressure control valve to maintain the system pressure at 60 psig. The reactor was charged with a supported chromium oxide catalyst.

[00121]   13.88 g/min HF and 6.05 g/min CFC-216aa were fed into a vaporizor. The gas mixture was conveyed to the reactor, and products were removed and fed into a distillation column to separate HCl, CFC-217ba and light components. It is to be understood that the Step III reaction can be carried out using a fluorine-containing gas other than HF.

[00122]   The heavier Step III reaction products were separated from the CFC-217ba reaction product. The CFC-217ba reaction product included unreacted $C_3Cl_2F_6$. The mass balance results are shown below in Table 9.

Table 9. Mass Balance Results

Total Feed Materials:	$C_3Cl_2F_6$ (99.7%) =	20.7 lbs
	HF =	2.0 lbs
Total Products Collected:	HCl =	2.588 lbs
	HF =	0.289 lbs
	C_3ClF_7 =	9.11 lbs
	$C_3Cl_2F_6$=	7.26 lbs
Recovery		84.8%

[00123]   As is demonstrated above in Table 9, approximately 85% of the reactants are recovered as products that can either be further refined, recycled or purified.

[00124]   Non-limiting example 15 demonstrates the impact of the catalyst selection on the process of the present invention.

Example 15: Comparison of Catalyst

[00125]   The Step III reaction was performed as described in Example 14 above with the exception that the catalyst parameters noted in Table 10 below were utilized. Over a 12-hour period, multiple reaction product samples were taken. The average C_3ClF_7 selectivity is shown in Table 10 below.

Table 10. Average C_3ClF_7 Selectivity % (12 hours average)

Chromium Oxide			Chromium Chloride	
Activated by method (a)	Activated by method (b)	Activated by method (c)	Activated by method (b)	Activated by method (c)
82.74	82.29	84.10	76.19	81.40

[00126]   As seen from these results, the Step III process according to the present invention selectively fluorinates the desired $C_3Cl_2F_6$ resulting in increased C_3ClF_7 production using catalysts of varying chemistry and activation.

[00127]   To further demonstrate the flexibility of fluorination according to the present invention, numerous catalysts were employed. These catalysts were prepared following the same general preparation methods detailed in examples 1 through 4 described above. These catalyst and reaction parameters are shown below in Table 11.

TABLE 11. $C_3Cl_2F_6$ to CFC-217ba with Different Catalyst Systems

Catalyst	Temp.(C)	Contact Time (sec)	Mole Ratio $C_3Cl_3F_5$	Conversion	Selectivity to CFC-217ba	CFC-13	CF-218	CFC-115	CFC-217ba	CFC-114	CFC-216aa	CFC-216ba	HCF-226da
NiCl₂/ZnCl₂/AC*	300	27.7	3.2	20.1	1.7	0.08	0.01	0.04	0.34	1.01	71.89	7.97	16.34
	400	29.6	3	46.5	8.6	18.25	3.81	0.16	3.97	6.81	45.21	8.32	5.81
	450	18.9	5.3	43.9	85	0.64	0.01	0.07	8.72	0.86	78.92	9.60	0.00
Activated Carbon	400	19.7	5.7	42.4	64.5	0.34	0.03	0.22	33.23	0.61	52.35	n/d	12.60
	450	18.4	5.3	28.7	77.1	0.60	0.03	0.05	17.02	0.50	78.86	n/d	1.44
	480	10.1	5	56.6	90.7	0.81	0.38	0.36	51.23	0.89	43.26	n/d	2.80
ZnCl₂/AC	300	10.4	6.5	21.0	3.3	0.01	0.00	0.01	0.69	0.64	71.20	7.80	18.89
	400	19.1	4.2	21.8	51.6	0.13	0.01	0.13	11.22	0.67	72.40	5.85	9.14
	450	9.2	5.2	14.6	55.7	0.81	0.00	0.09	6.67	0.61	79.36	8.74	2.58
	480	19.6	5	73.3	91.6	1.24	0.39	0.69	59.86	0.68	30.25	2.81	3.08
2% FeCl₃/AC	400	11.2	6.2	87.6	86.7	0.79	3.74	0.17	70.89	0.35	14.54	1.47	6.96
	450	10.3	6.2	99.9	35.5	6.88	6.69	1.92	64.62	6.88	0.22	0.91	3.07
	300	10.6	6.5	15.3	5.7	0.02	0.00	0.00	0.90	0.49	76.31	8.38	13.34
6% FeCl₃/AC	400	19.5	4.2	38.9	74.3	0.16	0.02	0.10	16.08	0.52	72.96	n/d	9.64
	450	19.5	4	48.4	86.2	0.61	0.16	0.29	35.58	0.60	57.24	n/d	4.90
	480	19.7	5	89.5	88.4	1.46	0.97	0.76	71.05	0.88	18.69	0.84	5.02
CrCl₃/AC	300	10.5	6.5	52.1	5	0.05	0.00	0.04	2.05	1.63	61.92	7.15	26.42
	400	20.0	5.7	34.5	71.2	0.44	0.04	0.42	29.85	3.27	59.86	n/d	5.31
	450	18.9	4	66.4	84.6	0.60	0.13	0.34	39.81	1.53	45.75	2.49	7.50
	480	18.8	3.8	74.2	84.4	1.81	0.47	0.77	58.97	1.27	26.32	2.32	6.58
KF/AC	400	19.6	4.2	19.6	34.6	0.23	0.01	0.09	15.10	0.21	63.71	3.11	15.33
	450	19.6	4	84.3	63.7	1.46	0.40	0.46	77.18	0.55	15.92	0.72	1.47
	480	19.4	5	79.2	68.4	1.94	1.56	0.66	75.04	0.87	12.23	1.72	3.96
Chrome Gel ®**	400	16.1	2.5	35.2	36.75	3.46	0.07	2.39	12.93	n/d	64.82	n/d	n/d
	480	18.98	9.5	85.94	84.2	n/d	4.07	0.20	72.36	n/d	14.05	0.84	5.24

n/d = not detected
AC = Activated Carbon

[00128]   As the results of Table 11 demonstrate various catalysts and reaction parameters prove useful. Particularly useful are iron, zinc and chromium chloride catalyst systems.

[00129]   The reaction products of the Step III reaction can be purified according to another process of the present invention. A process of the present invention is provided for separating C-3 chlorofluorinated compounds from a halogenation reaction product. The halogenation reaction products contemplated in this invention include the reaction products of Step III described above. This reaction product will include chlorofluorinated compounds having at least three carbon atoms. According to one embodiment of the present invention, the halogenation reaction product includes CFC-217ba. Accordingly, a halogenation reaction product is provided which comprises C-3 chlorofluorinated compounds, HCl and HF. These types of halogenation reaction products will typically result from the halogen exchange of fluorine for chlorine on a chlorofluorocarbon.

[00130]   According to one embodiment of the present invention, the temperature of the halogenation reaction product is lowered sufficiently to separate the reaction products into at least three phases, including a upper gas phase containing HCl, a top liquid phase containing HF and a bottom liquid phase containing essentially acid free C-3 chlorofluorinated compounds. The

temperature sufficient to separate the reaction product into at least three phases is from about 20°C to about 75°C. Preferably, the temperature is about 25°C. Like the separations previously described, the particular apparatus used for performing this separation is not critical. Examples of apparatus that would perform sufficiently include temperature regulated tanks and continuous phase separators.

[00131] The process according to the present invention allows for the continuous and/or batch separation of HF and HCl from C-3 chlorofluorinated compounds. This is desirous in any industrial halogenation reaction scheme or small scale reaction scheme because it is often necessary to remove HCl and HF from the reaction product. Typically, this is a costly endeavor, requiring the separate stripping of the HCl and subsequent distillation of the HF.

Example 16: Heterogeneous Phase Separation of C_3ClF_7:

[00132] The fluorination reaction of HF and $C_3Cl_2F_6$ comprised a reaction product stream containing approximately 40-45 weight % C_3ClF_7 and 50-55 wt % $C_3Cl_2F_6$ on an acid free basis. The reaction product was cooled and sent directly to a one gallon liquid phase separation tank. The vapor pressure of the mixture in the phase separator was 80 psig at 25°C. The reaction product separated into three phases. The top gaseous phase was primarily HCl gas. The bottom liquid organic phase was decanted off to be purified to produce essentially pure C_3ClF_7. The top

liquid HF rich phase can be decanted off and pumped directly back as recycled HF, but for purposes of this example, it was discarded. The bottom phase contained mainly organics which measured 54 weight % CFC-216 and 42 weight % C_3ClF_7. The breakdown of the bottom phase composition is shown below in Table 12:

Table 12. Contents of Bottom Phase of Heterogenous Separation

%HF	%HCl	%Organic
1.5	2.5	96.0

[00133]   The top vapor phase gas stream contained primarily HCl and was fed directly to a distillation column for simple distillation. The pressure was controlled for the entire system via this distillation pressure controller to distill HCl out the top. The HF phase composition is shown below in Table 13:

Table 13. Contents of Top Liquid Phase of Heterogenous Separation

%HF	%HCl	%Organic
89.24	4.20	6.56

[00134]   As Table 12 and 13 demonstrate, HF, HCl and organic fluorination reaction products can be efficiently separated in a one-step process. This process is extremely useful because it negates the high costs associated with expensive multi-step distillation and separation techniques.

[00135]   Once separated according to this invention the reaction compounds can be used as final products or returned to a reaction scheme for further

processing. According to the present invention the compounds thus separated have such high purity that they may proceed immediately to the next step without further purification.

[00136] In accordance with still another process of the present invention, a halogenated organic compound is provided to be contacted with H_2 and a catalyst to form a hydrodehalogenation reaction product. In a preferred embodiment the halogenated organic compounds are the Step III reaction products which include CFC-217ba. Accordingly, the halogenated organic compounds are premixed with hydrogen and contacted with a metal containing catalyst at sufficient temperature to produce a hydrodehalogenation reaction product. In still another embodiment the hydrodehalogenation reaction products include HFC-227ea. A reaction of this embodiment is shown below:

$$C_3$$

$$_0ClF_7 + H_2 \rightarrow HFC\text{-}227ea + HCl$$
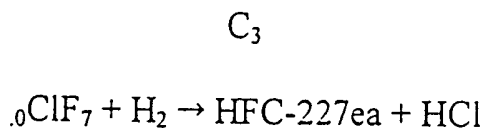
[00137] A slight molar excess of H_2 can be used if desirable but is not necessary. The H_2:halogenated organic compound molar ratio is in the range of about 0.2:1 to about 10:1, optimally about 1.2:1.

[00138] Referring now to **Fig. 6**, the hydrodehalogenation is performed in fixed bed reactor 42 containing a suitable catalyst, such as palladium on a

refractory oxide support, such as alumina or other suitable supports, in which case the reactor is operated at a temperature of about 30°C to about 275°C, and preferably at about 185°C. Alternatively, a ferric chloride ($FeCl_3$) catalyst on a solid support, such as active carbon can be used in which case the reactor is operated at a temperature of about 200°C to about 600°C, and preferably at about 450°C to about 500°C.

[00139] The pressure in reactor 42 should be in the range of about 14 psig to about 200 psig, and preferably about 100 psig. The reaction is largely insensitive to pressure in the range of 0-100 psig, however, reaction selectivity is slightly favored by lower pressures. Residence time in reactor 42 should be in the range of about 10 seconds to about 90 seconds, and preferably about 15 to about 60 seconds.

[00140] While any hydrodehalogenation catalyst could be used, the most active catalysts, such as Pt and Pd, are good selections because, in addition to the desired products, they lead to the addition of hydrogen across any double bond present or to the substitution of hydrogen for chlorine. Catalysts which may be utilized include, as charged to the reactor, common hydrogenation catalysts such as Cu, Ni, Cr, Ru, Rh or combinations thereof. It is not critical whether the catalysts are supported or not. However, supports which are unreactive to halocarbons, HF,

and oxygen at hydrogenation temperatures up to 100°C higher such as metal fluorides, carbon, and titania, may be used.

[00141]   Referring now to Fig. 7, the high cost of noble metals led to concerns regarding catalyst lifetime. Initial testing demonstrated that the catalyst is somewhat fragile with activity dropping off within 5 days. Fortunately, it has been discovered that the addition of a small amount of water to the reaction stream extended catalyst lifetime. The addition of water allows the catalyst to perform in excess of 15 days with no apparent loss of activity. The chemistry is not particularly sensitive to the amount of water present above a minimum of 0.8%. It has been determined that this process enhancement will test favorably with various catalysts. In one particular embodiment, water was added to the H_2 and halogenated organic compound and contacted with a catalyst. The additional water is from about 0.04 to about 12 percent by weight of the halogenated organic compound, and preferably, about 0.8 percent by weight of the halogenated organic compound. The previous description of the preferred embodiments will now be further demonstrated by way of non-limiting examples.

Example 17: Step IV ($C_3ClF_7 \rightarrow$ HFC-227ea:

[00142]   A 0.5" I.D. x 24" long stainless steel pipe heated by an electric heater was used to combine materials as described Tables 14 and 15 and **Fig. 7** below.

The crude organic gas was then washed with water to remove acids and the gas was analyzed by gas chromatography. Table 14 demonstrates the results of this selective hydrodehalogenation with varying catalysts at varying temperatures. Table 15 demonstrates the extension of catalyst life according to the present invention.

	Metal Catalyst Loading	Support	Additive	Contact time(s)	H2/C3ClF7	Temp (C)	% Results Conversion	HFC-227ea Selectiv
D i f f e r e n t S u p p o r t s / L o a d i n g	5% Pd	Activated Carbon		16.6	1.5	150	5.8	67.5
						180	16.4	69.5
	1% Pd	Activated Carbon		19.1	2	150	12.2	83.6
						180	47.9	89.8
						200	78.8	91.2
						225	96.8	87.6
						250	99.8	87.0
	1% Pd	Activated Carbon		36.7	1.8	150	26.7	83.5
						180	67.3	90.2
						200	72.0	90.0
						225	92.8	87.1
	0.5% Pd	Activated Carbon		15.4	1	150	3.1	74.4
						180	5.8	66.9
						200	9.6	75.8
	0.5% Pd	Activated Carbon		20.3	2.1	250	45.8	90.2
						275	68.7	88.2
						300	85.5	86.1
						325	95.5	80.0
	2.0% Cu/0.6% Pd	Activated Carbon		18.6	2	150	13.4	86.4
						180	50.8	89.3
						200	74.8	87.9
						225	87.6	83.7
						250	97.7	80.7
	2.0% Cu/0.6% Pd	Activated Carbon		37	1.8	180	42.7	87.8
						200	67.5	85.4
						225	83.4	85.9
						250	98.3	83.4
	2.0% Cu/0.6% Pd	Activated Carbon		10.2	2.4	150	7.1	46.8
						180	15.3	67.5
						200	28.2	76.9
						225	54.0	78.5
						250	80.0	77.9
						275	95.0	75.9
Different Metals	0.5% Ru	Alumina		22.4	1.3	150	2.5	22.4
						180	4.0	32.5
						200	5.0	39.4
	0.5% Rh	Alumina		23.6	1.5	150	12.9	67.1
						180	26.0	77.5
						200	26.6	83.6
	0.5% Pt	Alumina		23.1	1.5	150	2.8	44.5
						180	6.1	50.8
						200	14.3	80.3

Additives	0.5% Pd	Alumina	4.4% H20	21.9	1.4	180	63.1	98.1
	0.5% Pd	Alumina	1.8% H20	21.9	1.4	180	73.8	97.2
	0.5% Pd	Alumina	none	22.1	1.4	180	59.5	96.9
	0.5% Pd	#1310 – Alumina	none	21	1.4	180	96.6	95.7

[00143]   As Table 14 demonstrates, the selectivity of the present invention is substantially the same when performed at less than optimum temperature parameters. This allows for the selective production of selected isomers.

[00144]   Table 15 and **Fig. 7** demonstrate the catalyst life extension effectiveness of the present invention at varying levels of water addition. All conversions represented in Table 15 were performed at 180°C with a H_2 to C_3ClF_7 molar ratio between 0.9–1.5:1, a contact time of 20-30 seconds over a 0.5% Pd on Al catalyst.

Table 15. Catalyst Life Extension

450 ppm H2O	RUN TIME (days)	% CONVERSION C_3ClF_7	% SELECTIVITY HFC-227ea
	0.1	94.90	97.31
	0.2	93.87	97.31
	0.3	84.70	97.13
	0.96	80.90	97.92
	1.03	79.94	99.35
	1.05	79.98	96.91
450ppm H2O	RUN TIME (days)	% CONVERSION C_3ClF_7	% SELECTIVITY HFC-227ea
	0.1	93.67	95.61
	0.7	96.63	96.00
	0.8	95.53	95.79
	1.1	90.69	97.30
	1.7	78.82	97.15
	2.1	81.26	97.72
	3.0	49.15	95.84
	4.1	44.07	78.73

0.29% H2O	RUN TIME (days)	% CONVERSION C_3ClF_7	% SELECTIVITY HFC-227ea
	0.1	95.81	96.09
	0.3	98.40	95.54
	1.2	98.36	96.40
	1.3	98.40	96.44
	1.3	98.31	96.26
	1.3	96.58	96.13
	4.1	96.53	96.30
	4.2	95.88	95.76
	4.3	95.87	95.89
	4.3	95.77	95.74
	5.0	96.48	95.78
	5.1	94.84	95.79
	5.2	92.59	95.36
	5.3	91.89	97.39
	6.2	89.60	97.32
	6.3	91.18	97.44
	6.3	90.91	98.14
	7.0	85.48	97.10
	7.1	83.84	97.22
	7.3	79.20	97.20
	7.3	77.89	97.13
	8.0	69.32	97.10
	8.2	71.62	97.04
	8.3	76.70	97.17
	8.3	80.16	97.50
	11.0	60.41	96.61
	11.0	58.41	96.41
	11.2	56.68	96.36
	11.9	57.05	96.40
	12.1	55.97	96.35
	12.3	55.96	96.33
	12.9	54.04	96.22
	12.9	54.30	96.22

0.8% H2O	RUN TIME (days)	% CONVERSION C_3ClF_7	% SELECTIVITY HFC-227ea
	0.0	90.10	94.47
	0.7	93.60	95.35
	0.8	94.19	95.81
	1.0	92.39	95.65
	1.9	99.60	96.96
	2.0	96.71	96.59
	4.7	99.73	96.00
	4.8	98.96	97.89
	5.0	97.93	96.00
	5.0	98.16	96.10
	5.8	98.27	96.08
	6.0	97.96	95.95
	6.9	96.76	95.64
	7.8	90.03	94.96
	8.7	96.52	95.42
	9.0	94.70	95.20
	11.7	97.19	97.90
	12.0	93.80	97.45

12.8	91.60	97.51
13.0	91.49	97.48
14.0	96.78	96.04
15.0	95.11	95.83
15.1	94.57	94.96

[00145]   To demonstrate the increased catalyst life utilizing water in the

dehydrohalogenation reaction according to this invention, catalyst, H_2 and C_3ClF_7

were prepared as described above with the addition of water as demonstrated in

Table 17 above. It is clearly evident, particularly from **Fig. 7**, that the addition of

water significantly increases catalyst life without affecting the conversion and

selectivity.

[00146]   Like Steps I, II and III control and reduction of the undesired isomer

in Step IV can be achieved by selective reaction. Example 18 demonstrates this

isomer control thoughout the entire process when Steps I-IV are utilized in

sequence. Of course the combination of the steps of the present invention include

the following combinations: I, II and III (production of essentially isomerically

pure CFC-217ba); and I, II and IV (production of essentially isomerically pure

HFC-227ea); and I and II (production of essentially isomerically pure CFC-216aa).

Data from a variety of sources has all shown that even at 90% conversion there is

effective reduction of the isomer content.

Example 18: Steps I-IV:

[00147]   Reactors of the type described in the previous example were placed in series and prepared as previously described. The specific reaction conditions are denoted in the Table 16 below.

Table 16. Isomer Selectivity in Steps I-IV

Control of the Formation of CFC-216aa
Steps I and II

Chromium Oxide Catalyst	Reaction Conditions						Results (%)		
	Step I Reactor Temperature (C)	HF/Cl$_2$/Propane	Contact Time (s)	Step II Reactor Temperature (C)	Additional HF Added (mole)	Contact Time (s)	CFC-216aa	CFC-216ba	Selectivity to Usable F-Compound
A	200	5/8.1/1	15.3	450	10.3	4.85	54.3	13	91.2
B	200	5.22/8.78/1	10.9	450	12	8.9	56.8	N/D*	96.3

Isomer Reductions
Step III: As a Function of Conversion

Chromium Oxide Catalyst	Reaction Conditions				Results (%)					
	Reactor Temperature (C)	Contact Time (s)	HF/HFC-216aa	Starting % CFC-216ba	Conversion	Selectivity	CFC-216aa	CFC-216ba	CFC-217ba	CFC-217ca
A	450	16	4.2	1.34	38	56	66.17	0.56	16.12	0.023
B	480	14	3.7	1.34	48	71	55.07	0.55	30.47	0.13
C	550	13.5	6	1.34	90	87	11.73	0.17	79.15	0.47

Step IV: As a Function of Conversion
All Runs: 0/5% Pd/Al, Contact Time 21 sec, H$_2$:CFC-217ba 1.4:1

Starting Material % Composition:
CFC-217ba 99.82378
CFC-217ca 0.03389

Reaction Conditions	Results (%)				
Reactor Temperature (C)	Conversion	CFC-217ba	CFC-217ca	HFC-227ea	HFC-227ca
80	1.27	98.72826	0.03504	1.14277	0.0022
100	8.64	91.3592	0.03461	8.45215	0.00538
125	43.53	56.46954	0.0343	43.2857	0.00871
150	72.43	27.57251	0.03347	72.12256	0.01052
185	98.27	1.73023	0.01784	97.29827	0.02215

Starting Material % Composition:
CFC-217ba 97.25107
CFC-217ca 1.07103

Reaction Conditions	Results (%)				
Reactor Temperature (C)	Conversion	CFC-217ba	CFC-217ca	HFC-227ea	HFC-227ca
80	4.06	95.93715	1.10679	1.62392	0.00619
100	12.14	87.86218	1.09772	9.20849	0.01684
125	51.66	48.342	1.08432	48.59731	0.08311
150	83.01	16.99374	0.93024	79.81299	0.20022
185	97.26	2.74047	0.60435	93.62701	0.5128
200	98.99	1.01341	0.4536	94.3088	0.67959

*n/d = Not detected

[00148]   As Table 16 above demonstrates, the selectivity for a desired isomer

at each step carries through when the steps are combined. It is apparent that the

four step process may likewise produce HFC-227ea via three steps by performing

heretofore, Step IV following Step II. As shown above in Table 16 CFC-217ba is

produced following Step II.

[00149]   According to another aspect of the present invention, a process is

provided for the separation of a mixture of isomers of HFC-227ea and HFC-227ca.

This mixture can come from different sources, however, it is contemplated the

mixture will stem from a hydrodehalogenation reaction as described above.

According to one embodiment of the present invention a mixture of these isomers

is combined with a chlorofluorocarbon. Preferably, the chlorofluorocarbon is

C_3ClF_7. This solution comprising the HFC-227 isomers and the

chlorofluorocarbon are fed to a multiple stage distillation column operated under

conditions such that HFC-227ea can be effectively distilled as a pure isomer.

Distillation as it is known to those skilled in the art it is a separation process in

which a liquid is converted to a vapor and the vapor then condensed to a liquid.

The latter is referred to as the distillate and the liquid material being vaporized is

the charge or distillant. Distillation is thus a combination of the evaporation, or

vaporization, and condensation.

[00150]   The usual purpose of distillation is purification or separation of the

components of the mix. This is possible because the composition of a vapor is

usually different from that of the liquid mix from which it is obtained. Alcohol has

been so purified for generations to separate it from water, fuel oil, and aldehydes .

produced in the fermentation process. Gasoline, kerosene, fuel oil, and lubricating

oil are produced from petroleum by distillation. It is the key operation in removing

salt from sea water. Regrettably, isomeric mixtures cannot typically be separated

by distillation.

[00151]   Embodiments of the present isomer separation process include the use

of a ratio of chlorofluorocarbon to HFC-227ea from about 0.1 to about 10 and

preferably about 1 to about 7. Upon distillation of this mixture essentially pure

HFC-227ea is recovered as the distillate. The apparatus necessary to conduct this

process will be apparent to those skilled in the art. Fractional distillation columns

known in the industry will be readily useful to perform the process of the present

invention.

<u>Example 19: Distillation Separation of HFC-227ea from HFC-227ca:</u>

[00152]   To demonstrate the separation of HFC-227 isomers, a standard

distillation apparatus was utilized and configured according to the parameters

shown in Tables 17 and 18 below. As indicated, Table 17 demonstrates distillation

with a chlorofluorocarbon and Table 18 demonstrates distillation without a

chlorofluorocarbon.

Table 17. Distillation with C₃ClF₇

Column Conditions

Pressure (psig)	Temperature (°C)			Take Off (g/min)		
	Overhead	Bottom	Feed (g/min)	Overhead	Bottom	Reflux Ratio
61.8	29.4	36	2.93	2.21	0.45	25

Seperation Results-GC Profiles

	HFC-134a	FC-218	HFC-227ca	HCFC-124	HFC-227ea	HFC-236fa	Unknown	CFC-217ba	CFC-217ca
Feed	0.00258	0.00987	0.07504	0.01	83.33046	0.159881	0.11694	16.11326	0.14152
Overhead Take Off	0.00295	0.00392	0.01548	nd	99.97741	nd	nd	0.00573	nd
Bottom Take Off	nd	nd	0.12677	0.01923	57.10056	0.45827	0.30565	41.63464	0.35488

nd = not detected

Ratio HFC-227ea/HFC-227ca	Feed	1110
	Overhead	6458
	Bottom	450
Isomer Reduction Ratio (Overhead/Feed)		5.8

Table 18. Distillation without C_3ClF_7

Column Conditions

Pressure (psig)	Temperature (°C)		Feed (g/min)	Take Off (g/min)		Reflux Ratio
	Overhead	Bottom		Overhead	Bottom	
45.5	21.8	22.4	3.591	3.461	0.45	23

Seperation Results-GC Profiles

	HFC-134a	FC-218	HFC-227ca	HCFC-124	HFC-227ea	HFC-236fa	Unknown	CFC-217ba	CFC-217ca
Feed	0.00296	0.0687	0.0271	nd	99.95139	nd	nd	0.00928	nd
Overhead Take Off	0.00328	0.00671	0.01195	nd	99.98003	nd	nd	nd	nd
Bottom Take Off	nd	nd	0.07773	nd	99.86733	nd	nd	0.0549	nd

nd = not detected

Ratio HFC-227ea/HFC-227ca	Feed	3688
	Overhead	8367
	Bottom	1285
Isomer Reduction Ratio (Overhead/Feed)		2.3

[00153]   As shown in Tables 17 and 18, the addition of a chlorofluorocarbon significantly increases the ability, through distillation, to separate the isomers of HFC-227.

[00154]   The present invention also provides a process that selectively destroys undesired isomers, thereby increasing the overall isomeric purity in a mixture of isomers. According to one embodiment, this process includes providing a mixture of C-3 chlorofluorinated isomers. In another embodiment of the present invention, the C-3 chlorofluorinated isomers are CFC-216aa and CFC-216ba. In still another embodiment of the present invention, the C-3 chlorofluorinated compound isomers

are CFC-217ba and CFC-217ca. Other isomer mixtures that can be purified according to the present invention will be apparent to those skilled in the art.

[00155]   In accordance with the present invention, chlorofluorinated isomers are heated in the presence of a catalyst to a sufficient temperature to reduce the amount of at least one of the chlorofluorinated isomers. The isomers are heated in the presence of a catalyst in like fashion to the reaction Steps I, II, and III described above. According to one embodiment the catalyst used is a chromium containing catalyst. A suitable temperature to increase isomeric purity has been found to be from about 250°C to about 350°C. A more preferred temperature is about 280°C. By way of non-limiting example embodiments of this invention will now be demonstrated.

Example 20: Selective destruction of CFC-216ba:

[00156]   In accordance with the present invention, a mixture of CFC-216aa and CFC-216ba was provided having a relative ratio of CFC-216aa to CFC-216ba of 96:1. This mixture was heated in the presence of a pre fluorinated Chrom-gel® (provided by Englehard) catalyst at various temperatures outlined below with the results shown in Table 19 below.

Table 19. Selective Destruction of CFC-216ba Isomer

Reaction Temperature(°C)	Relative Ratio of CFC-216aa:CFC-216ba
325	257:1
250	325.03:1
250	309.53:1

[00157]   As can easily be seen from Table 19 the process according to the present invention effectively doubled the ratio of preferred isomer, CFC-216aa, to the undesired isomer, CFC-216ba.

[00158]   To demonstrate still another embodiment of the present invention, non-limiting example 21 is provided.

Example 21: Selective Destruction of CFC-217ca:

[00159]   In accordance with the present invention, a mixture of CFC-217ba and CFC-217ca was provided having a relative ratio of CFC-217ba to CFC-217ca of

81:1. This mixture was heated in the presence of a pre-fluorinated Chrom-gel®

catalyst at various temperatures outlined below with the results shown in Table 20

below.

Table 20. Selective Destruction of
CFC-217ca Isomer

Reaction Temperature(°C)	Relative Ratio of CFC-217ba:CFC-217ca
250	252.79:1
280	548.11:1

[00160]   As can easily be seen from Table 20, the process according to the

present invention effectively at least doubled the ratio of the preferred isomer,

CFC-217ba, to the undesired isomer, CFC-217ca and in some instances more than

quadrupled the ratio. Once purified in this fashion the resulting isomer is an

excellent reactant for hydrodehalogenation according to Step IV of the present

invention.

[00161]   In keeping with the selective destruction process previously described,

a process for selectively halogenating specific isomers within an isomeric mixture

is also provided. Isomer selective reactions play an important role when isomerically pure products are desired. According to one embodiment of the present invention a mixture of C-3 fluorinated isomers is provided and these isomers are contacted with Cl_2 in the presence of a catalyst at a sufficient temperature to halogenate at least one isomer.

[00162]   According to one embodiment of the present invention the mixture of C-3 fluorinated isomers contains HFC-227ea and HFC-227ca. It is contemplated that other hydrohalogenated compounds may be selectively halogenated according to this invention as well. Hydrohalogenated compounds suited for selective halogenation according to this invention will be obvious to those skilled in the art.

[00163]   According to still another embodiment of the present invention the catalyst is activated carbon. The specific type and preparation of the catalyst used to selectively halogenate are consistent with those catalysts described above in Steps I-IV.

[00164]   One aspect of the invention provides for the heating of the isomeric mixture to a sufficient temperature. According to one embodiment the temperature is from about 200°C to about 350°C. According to a more preferred embodiment, the temperature is about 300°C.

[00165]   According to still another embodiment of the present invention the

molar ratio of Cl_2 to the isomeric mixture is from about 0.16:1 to about 3:1 and

preferably about 2.5.

[00166]   By way of non-limiting example 22, embodiments of the present

invention will now be demonstrated.

Example 22: Selective Halogenation of HFC-227ea:

[00167]   The specific quantities and types of reactants and the condition of the reactor utilized to demonstrate this invention are shown in Table 21 below. The reaction products were monitored for the isomers of CFC-217.

Table 21. Selective Chlorination of HFC-227ea

Starting Material % Composition:
CFC-227ea 99.8678
CFC-227ca 0.0749

Activated Carbon	Reaction Conditions			Results (%)			
	Reactor Temperature (C)	Contact Time (s)	Cl2/HFC-227 Molar	Conversion	Selectivity	CFC-227ca	CFC-217ca
	250	13.3	2.01	24.49	98.85	0.0628	0.0219
	300	12.8	1.81	54.46	98.91	0.064	0.0223
	325	11.9	1.48	48.15	96.78	0.0744	0.0217
	325	21.9	2.69	98.91	97.91	n/d*	0.0767
	350	13.2	1.97	65.51	96.2	0.0548	0.0281
	325	22.3	2.91	98.14	98.25	0.0063	0.0751
	200	38.5	0.16	3.23	71.21	0.0981	0.0055
	300	21.8	0.55	44.81	96.51	0.0701	0.0211

*n/d = non-detectable

Starting Material % Composition:
CFC-227ea 99.5013
CFC-227ca 0.1411

Activated Carbon	Reaction Conditions			Results (%)			
	Reactor Temperature (C)	Contact Time (s)	Cl2/HFC-227 Molar	Conversion	Selectivity	CFC-227ca	CFC-217ca
	300	16.3	0.174692697	18.3	96.8	0.1255	0.0113
	300	15.8	0.34	46.8	98.6	0.0899	0.0414
	300	14.8	0.328435145	55.6	98.5	0.0829	0.0531
	300	26.9	0.84	79.2	98.7	0.0341	0.093

[00168] As Table 21 demonstrates, the present invention can be used to even further reduce the content of the undesired isomer. It is contemplated that once reduced the more isomerically pure reaction product can be recycled or further refined.

[00169] Additional objects, advantages, and other novel features of the invention will become apparent to those skilled in art upon examination of the foregoing or may be learned with practice of the invention. The foregoing description of the preferred embodiments of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Obvious modifications or variations are possible in the light of the above teachings. Embodiments were chosen and described to provide the best illustrations of the principals of the invention and their practical application, thereby enabling one of ordinary skill in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally and equitably entitled.